Towards the electron EDM search: Theoretical study of HfF^+

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We report first *ab initio* relativistic correlation calculations of potential curves for ten low-lying electronic states, effective electric field on the electron and hyperfine constants for the $^3\Delta_1$ state of cation of a heavy transition metal fluoride, HfF^+, that is suggested to be used as the working state in experiments to search for the electric dipole moment of the electron. It is shown that HfF^+ has deeply bound $^1\Sigma^+$ ground state, its dissociation energy is $D_e = 6.4$ eV. The $^3\Delta_1$ state is obtained to be the relatively long-lived first excited state lying about 0.2 eV higher. The calculated effective electric field $E_{\rm eff} = W_d|\Omega|$ acting on an electron in this state is 5.84×10^{24}Hz/(e·cm).

Introduction. The search for the electric dipole moment (EDM) of the electron, d_e or eEDM below, remains one of the most fundamental problems in physics. Up to now only upper limits were obtained for $|d_e|$. The tightest bound on d_e was obtained in the experiment on the Tl atom [1], which established an upper bound of $|d_e| < 1.6 \times 10^{-27}$ e·cm (e is the charge of the electron). It seems unlikely that experiments on atoms can give tighter bounds. Molecular systems, on the other hand, provide a way for much enhanced sensitivity, since the effective intramolecular electric field acting on electrons in polar molecules can be five or more orders of magnitude higher than the maximal field available in the laboratory [2, 3, 4].

The new generation of the eEDM experiments, employing polar heavy-atom molecules, is expected to reach sensitivity of 10^{-30}–$10^{-28} e$·cm/$\sqrt{\rm day}$ (e.g., see [5]). Their results are expected to dramatically influence all the popular extensions of the standard model, in particular supersymmetry, even if bounds on the P,T-odd effects compatible with zero are obtained (see [6, 7] and references therein). These studies include the beam experiments carried out on YbF molecular radicals by E. Hinds group at Imperial College, London [5], and the vapor cell experiment on the metastable $a(1)$ state of PbO prepared by the group of DeMille at Yale University (see [8] and references therein). New ways of searching for eEDM, using trapped cold molecular cations, were investigated during last two years at JILA by E. Cornell group. The first candidate was HI^+ [9], but subsequent estimate [10] and accurate calculations [11] have showed that the cation has rather small $E_{\rm eff}$ (see below). Then some more motivated candidates were considered, HfH^+ [12], HfF^+ [13] etc., having, possibly, working $^3\Delta_1$ as the ground or at least long-lived first excited state. Even experimental study of spectroscopic properties for this cation is a very difficult problem and there are no such data measured up to date though they are required already to analyze basic stages of the eEDM experiment [13]. In turn, the modern relativistic computational methods can now give reliable answers on almost all the questions of interest even for compounds of heavy transition metals as is in our case. So, the goal of the present paper is a theoretical study of required spectroscopic properties, $E_{\rm eff}$ and hyperfine structure of HfF^+ as a candidate for the eEDM experiment. Such a complete analysis is the first one performed for the given kind of molecules.

$E_{\rm eff}$, hyperfine structure and working state in HfF^+. One of the most important features of such experiments is that the knowledge of the effective electric field, $E_{\rm eff}$, seen by an unpaired electron is required for extracting d_e from the measurements. $E_{\rm eff}$ can not be obtained in an experiment, rather, electronic structure calculations are required for its evaluation. It is presented by the expression $E_{\rm eff} = W_d|\Omega|$, where W_d is a parameter of the P,T-odd molecular Hamiltonian that is given in Refs. [4, 14, 15]

$$W_d = \frac{1}{\Omega d_e}\langle\Psi|\sum_i H_d(i)|\Psi\rangle \ , \qquad (1)$$

where Ψ is the wavefunction for the working $^3\Delta_1$ state, and $\Omega = \langle\Psi|\boldsymbol{J}\cdot\boldsymbol{n}|\Psi\rangle = \pm 1$, $\boldsymbol{J}$ is the total electronic momentum, $\boldsymbol{n}$ is the unit vector along the molecular axis directed from Hf to F,

$$H_d = 2d_e \begin{pmatrix} 0 & 0 \\ 0 & \boldsymbol{\sigma E} \end{pmatrix} \ , \qquad (2)$$

$\boldsymbol{E}$ is the inner molecular electric field, $\boldsymbol{\sigma}$ are the Pauli matrices. Recently, the $E_{\rm eff}$ value for the $^3\Delta_1$ state was estimated in the scalar-relativistic approximation by Meyer *et al.* [16] and the method used for calculation of $E_{\rm eff}$ is close in essence to that developed by us earlier [17] and applied to first two-step calculations of the PbF molecule [14, 17]. In the present work, a more reliable value of $E_{\rm eff}$ is calculated using the advanced two-step techniques developed by us later [18, 19, 20, 21]. The hyperfine constants for ^{177}Hf and ^{19}F nuclei ($A_\parallel$[Hf] and $A_\parallel$[F]) for the $^3\Delta_1$ state of HfF^+ are also calculated. When the experimental value $A_\parallel$[Hf] is measured, it will provide an accuracy check for the calculated $E_{\rm eff}$ value. Both $A_\parallel$[Hf] and $A_\parallel$[F] values are useful for identifying HfF^+ by his spectrum from another species in the experiment. Moreover, preparation of the HfF^+ cations in the working state for the eEDM experiment, registration of eEDM

signals etc. requires the knowledge of spectroscopic properties. In particular, an open question is to clarify, which state is the ground one. If $^3\Delta_1$ is not the ground state, its radiative lifetime is also required. In the present work these data are obtained, though precise studying of the compounds with transition elements is a difficult problem for modern molecular theory. The needed spectroscopic information cannot be obtained now from other sources.

Methods and calculations. The 12-electron generalized relativistic effective core potential (GRECP) [22] simulating interaction with the explicitly excluded $1s$ to $4f$ electrons of Hf is used in 20-electron calculations of HfF^+. In 10-electron calculations which are substantially less time consuming, $5s$ and $5p$ spinors of hafnium and $1s$ orbital of fluorine are frozen from the states averaged over the nonrelativistic configurations $5d^26s^{0.6}6p^{0.4}$ for Hf^+ and $2s^22p^5$ for F and not treated explicitly. The generalized correlation atomic basis set (GCBS) [23, 24] $(12s16p16d10f10g)/[6s5p5d3f1g]$ is constructed for Hf. The ANO-L $(14s9p4d3f)/[4s3p2d1f]$ atomic basis set listed in the MOLCAS 4.1 library [25] was used for fluorine. The molecular orbitals are obtained by the complete active space self-consistent field (CASSCF) method [25, 26] with the spin-averaged part of the GRECP [27], i.e. only scalar-relativistic effects are taken into account at this stage. In the CASSCF method, orbitals are subdivided into three groups: inactive, active and virtual. Inactive orbitals are doubly occupied in all the configurations, all possible occupations are allowed for active orbitals, whereas virtual orbitals are not occupied. So, wave function is constructed as a full configuration interaction expansion in the space of active orbitals and both active and inactive orbitals are optimized for subsequent correlation calculations of HfF^+. Using the C_{2v} point group classification scheme, five orbitals in A_1, four in B_1 and B_2 and two in A_2 irreps are included into the active space. In 10-electron calculations, one orbital in the A_1 irreps (which is mainly $2s$ orbital of F) belongs to the inactive space. In 20-electron CASSCF calculations, the $5s$ and $5p$ orbitals of Hf and $1s$ orbital of F are added to the space of inactive orbitals.

Next, the spin-orbit direct configuration interaction (SODCI) approach [28, 29, 30] modified by our group to account for spin-orbit interaction in configuration selection procedure [31] with the selected single and double excitations from some multiconfigurational reference states ("mains") is employed on the sets of different ΛS many-electron spin- and space-symmetry adapted basis functions (SAFs). Details on features of constructing the reference space and selection procedure are given in Refs. [21, 31, 32].

Ten lowest states with the leading configurations $[...]\sigma_1^2\sigma_2^2$ ($^1\Sigma^+$), $[...]\sigma_1^2\sigma_2^1\delta^1$ ($^3\Delta_{1,2,3}$; $^1\Delta$), $[...]\sigma_1^2\sigma_2^1\pi^1$ ($^3\Pi_{0^-,0^+,1,2}$; $^1\Pi$) were calculated. Here σ_1 orbital is mainly formed by $2p_z$ orbital of F with admixture of $6p_z$ and $6s$ orbitals of Hf, σ_2 is mainly $6s$ orbital of Hf with admixture of $6p_z$ orbital of Hf, δ and π are mainly the $5d$ orbitals of Hf.

To obtain spectroscopic parameters, six points between 3.1 and 4.0 a.u. and point at 100 a.u. of the HfF^+ potential curves were calculated for ten lowest-lying states in 10-electron calculations and for four states in 20-electron ones. The 20-electron calculation is substantially more time-consuming and for the rest six states were calculated only for one point, 3.4 a.u., in the present study. Comparing the latter calculations with corresponding 10-electron ones the core ($5s^2, 5p^6$ shells of Hf and $1s^2$ shell of F) relaxation and correlation corrections to the T_e values, called "core corrections" below and in Table I, were estimated. The core properties $A_\parallel$ and $E_{\rm eff}$ were calculated only for the working $^3\Delta_1$ state at point 3.4 a.u., which is close to the equilibrium distance (see Table I). Before calculating core properties the shapes of the four-component molecular spinors are restored in the inner core region after the two-component GRECP calculation of the molecule. For this purpose the nonvariational one-center restoration (NOCR) method [17, 18, 20, 21, 27, 33] is applied.

Results and discussion. The results of calculations for HfF^+ spectroscopic parameters are presented in Table I. The first point to note is that the cation is deeply bound. Second important result is that the $^1\Sigma^+$ state appears to be the ground one and the working state, $^3\Delta_1$, is the first excited one. Besides, the excitation energy from $^1\Sigma^+$ to $^3\Delta_1$ is increased from 866 cm^{-1} to 1633 cm^{-1} after including the $5s$ and $5p$ shells of Hf and $1s$ shell of F to the relativistic correlation calculation. Excitation energies from $^1\Sigma^+$ to other calculated low-lying states are also increased. Note also that the values obtained in 10-electron calculations for lowest four states when just the core correction described above is taken into account are in a good agreement with the purely 20-electron calculations. (Note that accounting for correlation/relaxation of the $4f$-shell would be also desirable but it is too consuming and we expect it will result in smaller change of spectroscopic properties than that for the above core correction.) The SO splittings of the $^3\Delta$ and $^3\Pi$ states are mainly due to the SO splitting of the $5d$ shell of Hf:

$$\mathbf{H}_{ls}^{\rm so} = a \cdot (\mathbf{l}_{\rm 5d} \cdot \mathbf{s}_{\rm 5d}) \ , \qquad (3)$$

The atomic Dirac-Fock calculation of Hf^+ gives $\varepsilon_{5/2} - \varepsilon_{3/2} = 3173$ cm^{-1} $\Rightarrow$ $a = 1269$ cm^{-1}, where $\varepsilon_{5/2}$ and $\varepsilon_{3/2}$ are orbital energies of $5d_{5/2}$ and $5d_{3/2}$ states of Hf^+. The SO interaction (3) averaged over the $^3\Delta$ or $^3\Pi$ states is reduced to

$$\mathbf{H}_{LS}^{\rm so} = \mathcal{A} \cdot (\mathbf{L} \cdot \mathbf{S}), \qquad (4)$$

where $\mathcal{A} = 1269/2 = 635$ cm^{-1}, $\mathbf{L}$ and $\mathbf{S}$ are the orbital and spin momenta of HfF^+. The SO interaction (4) leads to splitting between components of the $^3\Delta$ and $^3\Pi$ states on 1269 and 635 cm^{-1}, correspondingly. It is in a good

TABLE I: Calculated spectroscopic parameters for HfF^+

State	R_e Å	T_e cm^{-1}	T_e with core correction[a]	w_e cm^{-1}	D_e cm^{-1}
10-electron calculation					
$^1\Sigma^+$	1.784	0	0	751	51107
$^3\Delta_1$	1.810	866	1599	718	
$^3\Delta_2$	1.809	1821	2807	719	
$^3\Delta_3$	1.807	3201	4324	721	
$^1\Delta_2$	1.814	9246	11519	696	
$^3\Pi_{0-}$	1.856	9466	11910	689	
$^3\Pi_{0+}$	1.854	9753	12196	699	
$^3\Pi_1$	1.860	10190	12686	687	
$^3\Pi_2$	1.856	11898	14438	703	
$^1\Pi_1$	1.870	12642	14784	679	
20-electron calculation					
$^1\Sigma^+$	1.781	0		790	51685
$^3\Delta_1$	1.806	1633		746	
$^3\Delta_2$	1.805	2828		748	
$^3\Delta_3$	1.804	4273		749	

[a] See paragraph "Methods and calculations" for details.

agreement with the splitting of the $^3\Delta$ state calculated in Table I but not with the $^3\Pi$ one because of the SO interaction with closely lying $^1\Delta$ and $^1\Pi$ states.

The calculated $A_\parallel$ and $E_{\rm eff}$ for the $^3\Delta_1$ state are presented in Table II. In opposite to $A_\parallel$[F], $A_\parallel$[Hf] and $E_{\rm eff}$ are not seriously changed when the outer core electrons are included into calculation. Such behavior of $A_\parallel$[F] is explained by the fact that fluorine can be considered with good accuracy as a closed shell subsystem (thus having $A_\parallel[\mathrm{F}] \approx 0$) in the $^3\Delta$ state, i.e. large compensation of contributions from orbitals with different projections of total electronic momentum for $A_\parallel$[F] takes place. Therefore, even small perturbation can seriously change the $A_\parallel$[F] value. Calculated $E_{\rm eff}$ is large and comparable with the corresponding value for the $a(1)$ state of the PbO molecule [21]. If one does not pay attention to the difference of signs our value is in 1.34 times larger than value obtained in the paper [16] in scalar-relativistic calculations. Our rather crude estimate of the $^3\Delta_1$ lifetime for the $^3\Delta_1 \to {}^1\Sigma^+$ transition is about 1/2 sec. This value is difficult for accurate calculations because of small absolute values of both transition energies and, particularly, transition dipole moments between those states whereas absolute errors are similar to those for other transitions.

Acknowledgments. This work is supported by the RFBR grant 06–03–33060. T.I. and A.P. are also supported by grants of Russian Science Support Foundation. A.P. is grateful for the grant of Governor of Leningrad district.

TABLE II: Calculated parameters $A_\parallel$[Hf] and $A_\parallel$[F] (in MHz) and $E_{\rm eff}$ (in 10^{24}Hz/$(e\cdot\mathrm{cm})$) for the $^3\Delta_1$ state of $^{177}Hf^{19}F^+$ at internuclear distance of 3.4 a.u.

$A_\parallel$[Hf]	$A_\parallel$[F]	$E_{\rm eff}$
10-electron calculation		
-1250	-33.9	5.89
20-electron calculation		
-1239	-58.1	5.84

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